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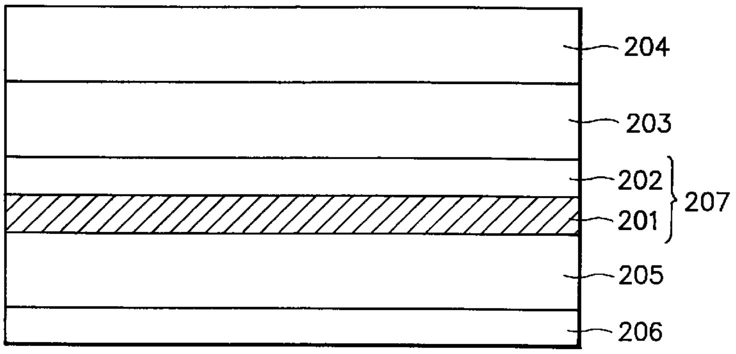
(54) A protective material for a semiconductor element, a semiconductor element provided with said protective material, and a semiconductor device provided with said semiconductor element

(57) A highly reliable surface covering material having a specific transparent resin layer formed of a resin containing a silane coupling agent in a state with no free material of said silane coupling agent for a semiconductor element or a semiconductor device, which is free of the occurrence of a separation, has a satisfactory heat resistance, and is hardly yellowed, and which enables the semiconductor element or semiconductor device to effectively its characteristics without being deteriorated, even when repeatedly used over a long period of time under severe environmental conditions with a high temperature and a high humidity.

FIG. 2



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Description

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to an improved, reliable protective material for a semiconductor element, a semiconductor element provided with said protective material, and a semiconductor device provided with said semiconductor element. More particularly, the present invention relates to an improved, reliable protective material which can be disposed at the surface of a semiconductor element including a photoelectric conversion element such as a solar cell element, specifically, which is suitable to use as a surface covering material disposed on the light incident side of said photoelectric conversion element. The present invention also relates to a semiconductor element including a photoelectric conversion element such as a solar cell element which is provided with said protective material, and a semiconductor device provided with said semiconductor element.

Related Background Art

In recent years, the societal consciousness for the problems relating to the environment and energy has been increasing all over the world. Particularly, heating of the earth because of the so-called greenhouse effect due to an increase of atmospheric CO_2 has been predicted to cause a serious problem. In view of this, there is an increased demand for a means of power generation capable of providing clean energy without causing CO_2 buildup.

Now, public attention has been focused on solar cells in order to meet such demand, because they can supply electric power without causing such a problem as above mentioned and are expected to be a future power generation source, and they are safe and easy to handle.

Such a solar cell includes single crystal silicon solar cells, polycrystal silicon solar cells, amorphous silicon solar cells (including microcrystal silicon solar cells), copper indium selenide solar cells, and compound semiconductor solar cells. Of these solar cells, various studies have been made on so-called thin film crystal silicon solar cells, compound semiconductor solar cells and amorphous silicon solar cells since their semiconductor active layer can be relatively easily formed in a large area and in a desired form and they therefore can be easily produced at a relatively low production cost.

Particularly, thin film amorphous solar cells, specifically, amorphous silicon solar cells, comprising an electrically conductive metal substrate, an amorphous silicon semiconductor active layer disposed on said metal substrate, and a transparent and conductive layer disposed on said semiconductor active layer have been evaluated as being the most advantageous among the conventional solar cells because their semiconductor active layer comprised of amorphous silicon (hereinafter referred to as a-Si) can be easily formed in a large area and in a desired form on a relatively inexpensive substrate with a low production cost and they are light and excel in shock resistance and flexibility, and in addition, they can be designed into a solar cell module in a desired configuration which can be used as a power generation source.

Now, in the case of an amorphous silicon solar cell having a semiconductor active layer comprising, for example, an a-Si thin film disposed on a glass plate as a substrate, light is impinged through the substrate side, and because of this, the glass plate can be designed to serve as a protective member. However, in the case of the aforementioned solar cell having the a-Si semiconductor active layer disposed on the metal substrate, because the metal substrate does not permit incident light to transmit therethrough, light is impinged through the side opposite the metal substrate, and therefore, it is necessary to dispose an appropriate transparent protective member on the side through which light is impinged such that it protects the solar cell element.

SUMMARY OF THE INVENTION

In the conventional semiconductor devices (including the conventional solar cell modules) having a photoelectric conversion element such as a solar cell element, the light incident side of the photoelectric conversion element is protected by a surface covering material comprising a transparent fluorine-containing polymer film comprised of a fluororesin or a fluororesin-containing composition as a surface protective member which is positioned at the outermost surface and a transparent thermoplastic resin as a filler which is positioned under the transparent fluorine-containing polymer film.

The fluorine-containing polymer film is often used in the above described manner, since it is advantageous in that it is satisfactory in terms of weatherability and water-repellency and serves to diminish a deterioration in the photoelectric conversion efficiency of the photoelectric conversion element caused due to a reduction in the transmittance of the surface protective member occurred when the protective member is yellowed or clouded as a result of the protective member having been deteriorated. As for the thermoplastic resin used as the filler in combination with the fluorine-containing polymer film, it is also often used since it is relatively inexpensive and suitable for protecting the photoelectric conversion element and it therefore can be used in a relatively large amount.

Now, description will be made of such semiconductor device (solar cell module).

FIG. 1 is a schematic cross-sectional view of an example of the solar cell module. In FIG. 1, reference numeral 101 indicates a transparent fluorine-containing polymer thin film layer as an outermost surface protective layer, reference numeral 102 a transparent thermoplastic resin layer which is situated under the fluorine-containing thin film layer 101, reference numeral 106 a solar cell element comprising a photovoltaic element 104 and a transparent resin thin film layer 103 disposed on the surface of said photovoltaic element, and reference numeral 105 an insulating layer. In this solar cell module, the solar cell element 106 is enclosed by the transparent thermoplastic resin layer 102 which serves as a filler.

Specifically, the fluorine-containing polymer thin film layer 101 comprises a fluororesin film selected from the group consisting of ETFE (ethylene-tetrafluoroethylene copolymer) film, PVF (polyvinyl fluoride) film, and the like. The transparent thermoplastic resin layer 105 comprises a thermoplastic resin selected from the group consisting of EVA (ethylene-vinyl acetate copolymer), EEA (ethylene-acrylic ester copolymer), and butyral resin. The transparent resin thin film layer 103 comprises comprises a resin film composed of an acrylic resin, a fluororesin, or an acrylic resin crosslinked with an inorganic polymer. The insulating layer 405 comprises an organic resin film such as nylon film, TEDLAR (trademark name, laminated aluminum foil), or the like.

In the above described solar cell module, the transparent thermoplastic resin layer 102 serves not only as an adhesive between the photovoltaic element 104 and the fluororesin film 101 as the surface protective layer but also as an adhesive between the photovoltaic element and the insulating layer 105. The transparent resin thin film layer 103 disposed on the photovoltaic element 104 serves to electrically isolating the photovoltaic element from outside the module. In addition, the transparent resin thin film layer 103 in combination with the transparent thermoplastic resin layer 102 serves as a filler of preventing the photovoltaic element 104 from being externally damaged and from being suffered from external shocks. The insulating layer 105 serves to reinforce the solar cell module while adding an appropriate rigidity thereto.

As for the solar cell module thus constituted, it is often configured so that it can be placed on the roof of a building or can be integrated with the roof of a building. In this case, it is necessary to meet the roofing standards prescribed in each country. The roofing standards sometimes includes the combustion test. In order to clear the combustion test, it is desired that the amount of EVA as a combustible resin used as the filler in the solar cell module is diminished as much as possible. However, when the amount of the EVA used in the solar cell module is simply diminished, a problem entails in that the performance of the surface covering material to protect the photovoltaic element is reduced as the the amount of the EVA used is diminished.

In order to solve this problem, there is known a manner wherein a transparent resin thin film layer composed of a fire-retarding or incombustible transparent resin is disposed in the surface covering material and the thickness of the EVA layer is thinned as desired whereby attaining an incombusibility for the solar cell module without reducing the performance of the surface covering material to protect the photovoltaic element. According to this manner, for instance, it is possible to attain a solar cell mode which can be classified into Class A in the combustion test in the standard UL 1703 of the U.S.A. that prescribes a solar cell module which can be used as a roofing.

Now, as for the above described fire-retarding or incombustible transparent resin thin film layer, it is usually formed of a resin obtained by crosslinking an acrylic resin or a fluororesin with isocyanate as a crosslinking agent. The coating composition containing isocyanate used for the formation of the fire-retarding or incombustible transparent resin thin film layer in this case includes a one-liquid type coating composition in which isocyanate is previously mixed with a resin (an acrylic resin or a fluororesin) and a two-liquid type coating composition in which the two materials (that is, the isocyanate and resin) are mixed immediately before the formation of a film.

The two-liquid type coating composition is problematic in that the apparatus used for the formation of a film using the two-liquid type coating composition is unavoidably complicated because the two materials are mixed immediately before the film formation and in addition, the pot life of the resin after the admixture is liable to shorten. For this reason, there is usually used the one liquid type coating composition, specifically, a one-liquid type coating composition using a so-called blocking isocyanate which is used in a manner of masking a highly reactive isocyanate group by a blocking agent and dissociating the blocking agent by virtue of a heat energy to regenerate the isocyanate group so as to dedicate for the crosslinking reaction for the resin. The blocking agent used for masking the isocyanate group in this case includes MEK (methyl ethyl ketone) oxime and -caprolactam. In the case where MEK oxime is used, a problem is liable to entail in that yellowing is occurred when the resulting coat film is subjected to heat treatment. Therefore, in the case where a transparent film is intended to form, -caprolactam is intentionally used.

Now, in the case of a solar cell module having a surface covering material constituted by a laminate comprising such a fire-retarding or incombustible transparent resin thin film layer as above described and a transparent thermoplastic resin layer composed of EVA for example, such problems as will be described in the following are liable to occur.

That is, when the solar cell module is continuously exposed to sunlight in outdoors over a long period of time, there is a tendency that the temperature of the surface of the photovoltaic element is heightened to 65 °C or more and the surface covering material is yellowed. This problem is liable to become significant in the case where the solar cell module is used while being integrated with the roof of a building wherein the temperature of the solar cell module is further heightened. This situation is occurred due to a cause that the blocking agent dissociated upon the crosslinking of the resin is remained in the coat film without being volatilized to react with an peroxide used for the crosslinking of the EVA or/and an acid generated upon the crosslinking of the EVA whereby causing the formation of a yellowed product of reducing the light transmissivity of the surface covering material, resulting in deteriorating the characteristics of the solar cell module.

In addition, when the solar cell module is continuously used in a severe outdoor atmosphere of high temperature and high humidity over a long period of time, a removal is liable to occur among the constituents of the surface covering material and also at the interface between the surface covering material and the photovoltaic element, resulting in not only deteriorating the characteristics of the solar cell module but also deteriorating the exterior appearance of the solar cell module.

In order to preventing the surface covering material from being yellowed due to heat degradation or light fatigue of the resin, the use of a primary antioxidant comprising a hindered phenol series antioxidant and a secondary antioxidant comprising a phosphorous series antioxidant in combination is known. However, the above described problems cannot be sufficiently solved by this manner of using aforesaid two antioxidants in combination.

In view of this, there is a demand for providing an improved solar cell module which is free of the above problems.

The present invention is aimed at eliminating the foregoing problems found in the conventional surface covering material for a semiconductor element and providing an improved, highly reliable surface covering material for said semiconductor element which is free of those problems in the prior art, wherein said surface covering material excels in adhesion with the semiconductor element and it is hardly yellowed and exhibits a desirable transmissivity without being deteriorated and without causing a separation between it and the semiconductor element even upon continuously exposing to a severe atmosphere with a high temperature and high humidity over a long period of time, and it enables to establish a highly reliable module of the semiconductor element which stably exhibits desirable module characteristics without being deteriorated even when it is continuously used under severe environmental conditions with a high humidity and with frequent changes in the environmental temperature over a long period of time.

The term "semiconductor element" in the present invention is meant to include a photoelectric conversion element including a solar cell element.

Another object of the present invention is to provide an improved, highly reliable surface covering material comprising a specific transparent resin layer for a semiconductor element, said transparent resin layer being formed of a resin containing at least a silane coupling agent.

A further object of the present invention is to provide a highly reliable semiconductor element provided with an improved, highly reliable surface covering material comprising a specific transparent resin layer, said transparent resin layer being formed of a resin containing at least a silane coupling agent.

A further object of the present invention is to provide a highly reliable semiconductor device provided with an improved, highly reliable surface covering material comprising a specific transparent resin layer and at least a transparent organic resin layer disposed on said specific transparent resin layer, said specific transparent resin layer being formed of a resin containing at least a silane coupling agent.

According to the present invention, there are provided such advantages as will be described in the following.

(1) There can be attained a highly reliable incombustible surface coat for a solar cell module. Particularly, by diminishing the amount of the combustible resin used in the surface covering resin material in the prior art, there can be attained a highly incombustible solar cell module.

(2) There can be attained a highly reliable surface coat excelling in heat resistance for a solar cell module. Particularly, there can be attained a highly reliable surface covering material comprising a coat film in which the amount of the residual blocking agent is slight and which is free of the problem found in the prior art in that the conventional surface covering material is yellowed upon the continuous use under environmental conditions with a high temperature.

(3) There can be attained a highly reliable surface coat excelling in moisture resistance for a solar cell module which effectively prevents moisture invasion, wherein the solar cell module does not suffer from a reduction in its characteristics due to moisture invaded.

(4) There can be attained a highly reliable surface coat excelling in adhesion for a solar cell module. Particularly, there can be attained a highly reliable surface covering material which is free of the problem found in the prior art in that the conventional surface covering material is liable to separate from the solar cell element (or the photoelectric conversion element) upon the continuous use under environmental conditions with a high temperature and high humidity, wherein the solar cell module does not suffer from a reduction in its characteristics due to such separation.

(5) There can be attained a highly reliable surface coat having an excellent electrically insulating property for a solar cell module. Particularly, there can be attained a highly reliable surface covering material which effectively prevents

an electric current generated from a solar cell element (or a photoelectric conversion element) from leaking the outside and always maintains the solar cell element in a state of being electrically isolated from the outside.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic cross-sectional view illustrating the constitution of a conventional solar cell module as a semiconductor device.

FIG. 2 is a schematic cross-sectional view illustrating the constitution of an example of a solar cell module as a semiconductor device according to the present invention.

FIG. 3 is a schematic cross-sectional view illustrating the constitution of an example of a photoelectric conversion element which can be used in the present invention.

FIG. 4 is a schematic cross-sectional view illustrating the constitution of another example of a solar cell module as a semiconductor device according to the present invention.

FIG. 5 is a schematic view for explaining the scratch resistance test which will be later described.

DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

The present invention is to eliminate the foregoing problems in the prior art and to attain the above described objects.

The present invention will be detailed while referring to the drawings.

FIG. 2 is a schematic cross-sectional view illustrating the constitution of an example of a solar cell module as a semiconductor device according to the present invention.

In FIG. 2, reference numeral 201 indicates a photovoltaic element (or a photoelectric conversion element), reference numeral 202 a transparent resin layer (comprising a transparent resin thin film), reference numeral 203 a transparent surface side filler (comprising a transparent organic high-molecular resin layer), reference numeral 204 a transparent film which is positioned at the outermost surface (this film will be hereinafter referred to as surface protective film or surface protective layer), reference numeral 205 a filler on the rear side of the photovoltaic element 201 (this filler will be hereinafter referred to as backside filler), and reference numeral 206 a back face protective film. Reference numeral 207 indicates a solar cell element comprising the photovoltaic element 201 and the transparent resin layer 202.

In the solar cell module shown in FIG. 2, light is impinged through the outermost surface film 204, and the light impinged passes through the outermost surface film 204, filler 203 and transparent resin layer 202 to arrive in the photovoltaic element 201. A photoelectromotive force generated in the photovoltaic element 201 is outputted through outputting terminals (not shown).

The photovoltaic element 201 comprises at least a semiconductor active layer as a photoelectric conversion member disposed on an electrically conductive substrate.

FIG. 3 is a schematic cross-sectional view illustrating the constitution of such photovoltaic element.

In FIG. 3, reference numeral 301 indicates an electrically conductive substrate, reference numeral 302 a back reflecting layer, reference numeral 303 a semiconductor active layer, reference numeral 304 a transparent and conductive layer, reference numeral 305 a collecting electrode (or a grid electrode), reference numeral 306a a power outputting terminal on the positive side, reference numeral 306b a power outputting terminal on the negative side, and reference numeral 307 an electrically connecting means.

As apparent from FIG. 3, the photovoltaic element comprises the back reflecting layer 302, the semiconductor active layer 303, the transparent and conductive layer 304, and the collecting electrode 305 disposed in this order on the electrically conductive substrate 301, wherein the outputting terminal 306a is electrically connected to the collecting electrode 305 by means of the electrically conductive paste or solder 307 and it is extending from the collecting electrode while being insulated by means of an insulating member (not shown), and the outputting terminal 306b is electrically connected to the electrically conductive substrate 301 by means of a solder (not shown). In this configuration, the positive side power outputting terminal and the negative side power outputting terminal may be changed into a negative side power outputting terminal and a positive side power outputting terminal depending upon the constitution of the semiconductor active layer.

The electrically conductive substrate 301 serves not only as a substrate for the photovoltaic element but also as a lower electrode. As for the electrically conductive substrate 301, there is no particular restriction as long as it has an electrically conductive surface. Specifically, it may be an electrically conductive member composed of a metal such as Ta, Mo, W, Al, Cu, Ti, or the like, or an electrically conductive member composed of an alloy such as stainless steel, or the like. Besides these, the electrically conductive substrate may comprise a carbon sheet or a Pb-plated steel sheet. Alternatively, the electrically conductive substrate may be a film or sheet made of a synthetic resin or a sheet made of a ceramic. In this case, the substrate is deposited with an electrically conductive film on the surface thereof.

The back reflecting layer 302 disposed on the electroconductive substrate 301 may comprise a metal layer, a metal oxide layer, or a two-layered structure comprising a metal layer and a metal oxide layer. The metal layer may comprise a metal such as Ti, Cr, Mo, W, Al, Ag, or Ni, or an alloy of these metals. The metal oxide layer may comprise a conductive metal oxide such as ZnO, SnO_2, or the like.

The metal layer and metal oxide layer as the back reflecting layer 302 may be formed by means of a conventional film-forming process such as resistance heating evaporation, electron beam evaporation, or sputtering.

The back reflecting layer 302 is desired to have a roughened surface in order to make incident light to be effectively utilized.

The semiconductor active layer 303 functions to conduct photoelectric conversion. The semiconductor active layer 303 may be composed of a non-single crystal silicon semiconductor material such as an amorphous silicon semiconductor material or polycrystalline silicon semiconductor material, or a compound semiconductor material. In any case, the semiconductor active layer comprised of any of these semiconductor materials may be of a stacked structure with a pn junction, a pin junction or a shottky type junction.

Specific examples of the compound semiconductor material are $CuInSe_2$, $CuInS_2$, GaAs, CdS/Cu_2S, CdS/CdTe, CdS/InP, $CdTe/Cu_2Te$, and the like.

The semiconductor active layer comprised of any of the above mentioned semiconductor materials may be properly formed by a conventional film-forming process. For instance, the non-single crystal silicon semiconductor active layer may be formed by a conventional chemical vapor phase growing process such as plasma CVD or light-induced CVD using proper film-forming raw material gas capable of imparting silicon atoms such as silane gas or a conventional physical vapor phase growing process such as sputtering or the like. The semiconductor active layer composed of a polycrystalline silicon semiconductor material may be formed by a conventional polycrystalline silicon film-forming process of providing a fused silicon material and subjecting the fused silicon material to film-making processing or another conventional polycrystalline silicon film-forming process of subjecting an amorphous silicon material to heat treatment.

The semiconductor active layer composed of any of the above mentioned compound semiconductor materials may be properly formed by means of ion plating, ion beam deposition, vacuum evaporation, sputtering, or electrolytic technique in which a precipitate is caused by way of electrolysis of a desired electrolyte.

The transparent and conductive layer 304 functions as an upper electrode. The transparent and conductive layer may comprise In_2O_3, SnO_2, In_2O_3-SnO_2 (ITO), ZnO, TiO_2, or Cd_2SnO_4. Alternatively, it may comprise a crystalline semiconductor layer doped with an appropriate impurity with a high concentration.

The transparent and conductive layer constituted by any of the above mentioned materials may be properly formed by means of resistant heating evaporation, electron beam evaporation, sputtering, spraying, or CVD.

The above described impurity-doped crystalline semiconductor layer as the transparent and conductive layer may be properly formed by a conventional impurity-diffusion film-forming method.

Now, for a stacked body (as a photovoltaic element) formed until the transparent and conductive layer 304, there is such an occasion that the electrically conductive substrate 301 and the transparent and conductive layer 304 are partially short-circuited due to an unevenness in the surface state of the electrically conductive substrate and/or an unevenness in the semiconductor active layer 303 occurred upon the formation thereof wherein the stacked body is in a state that a relatively large leakage current is flown in proportion to the voltage outputted, namely, in a state of being small in leak resistance (or shunt resistance). The stacked body (the photovoltaic element) having such defect is desired to be repaired in a defect-free state by eliminating the defect. This can be conducted, for example, in accordance with the defect-repairing manner described in U.S. Pat. No. 4,729,970. In this case, the defect-bearing stacked body is desired to be repaired to have a shunt resistance preferably in the range of from 1 $k\Omega.cm^2$ to 500 $k\Omega.cm^2$ or more preferably in the range of from 10 $k\Omega.cm^2$ to 500 $k\Omega.cm^2$.

For the purpose of efficiently collecting an electric current generated by virtue of a photoelectromotive force, the collecting electrode (or the grid eletrode) 305 may be disposed on the transparent and conductive layer 304. The collecting electrode 305 may be in the form of a stripe shape or comb shape.

The collecting electrode 305 may comprise a metal such as Ti, Cr, Mo, W, Al, Ag, Ni, Cu, or Sn, or an alloy of these metals. Althernatively, the collecting electrode may be formed of an electrically conductive paste or an electrically conductive resin. The electrically conductive paste can include electrically conductive pastes comprising powdery Ag, Au, Cu, Ni, or carbon dispersed in an appropriate binder resin. The binder resin herein can include polyester, epoxy resin, acrylic resin, alkyd resin, polyvinyl acetate, rubber, urethane resin, and phenol resin.

The collecting electrode 305 may be properly formed by means of sputtering using a patterning mask, resistance heating evaporation, or CVD. It may be also properly formed by a manner of depositing a metal film over the entire surface and subjecting the metal film to etching treatment to form a desired pattern, a manner of directly forming a grid electrode pattern by means of light-induced CVD, or a manner of forming a negative pattern corresponding to a grid electrode pattern and subjecting the resultant to plating treatment.

The formation of the collecting electrode using any of the above described electrically conductive pastes can be conducted in a manner of subjecting the electrically conductive paste to screen printing or a manner of fixing a metal wire to the screen-printed electrically conductive paste, if necessary, using a solder.

The outputting terminals 306a and 306b serve to output an electromotive force. The outputting terminal 306a is electrically connected to the collecting electrode 305 by means of the electrically connecting means 307 comprising an electrically conductive paste or a solder. The outputting terminal 306b is electrically connected to the electrically conductive substrate 301 by spot welding or soldering an appropriate metal body such as copper tab.

In general, there are provided a plurality of photovoltaic elements having the above constitution, and they are integrated in series connection or in parallel connection depending upon a desired voltage or electric current. It is possible to dispose the integrated body on an insulating member such that a desired voltage or electric current can be obtained.

Description will be made of the surface protective film 204 (or the surface protective layer).

The surface protective film 204 is positioned at the outermost surface of the solar cell module and because of this, it is required to excel in transparency, weatherability, water repellency, heat resistance, pollution resistance, and physical strength. In addition, in the case where the solar cell module is used in outdoors, it is required for the surface protective film to ensure that the solar cell module is of sufficient durability upon repeated use over a long period of time.

In order for the surface protective film to satisfy all these conditions, the surface protective film comprises a film composed of a highly transparent fluororesin. Specific examples of such highly transparent fluororesin are tetrafluoroethylene-ethylene copolymer (ETFE), polyvinyl fluoride resin (PVF), polyvinylidene fluoride resin (PVDF), polytetrafluoroethylene resin (TFE), tetrafluoroethylene-hexafluoropropylene copolymer (FEP), and polychlorotrifluoroethylene resin (CTFE). Of these fluororesins, PVF is most excellent in view of weatherability. And in view of weatherability and physical strength in combination, ETFE is most excellent.

In order to attain an improvement in the adhesion of the surface protective film 204 with the surface side filler 203, a given surface of the surface protective film to be contacted with the surface side filler is desired to subjected to surface treatment upon its lamination to the surface side filler. The surface treatment in this case can include corona discharging treatment and plasma treatment. In order for the surface protective film to have an improved physical strength, it is desired that the surface protective film comprises an oriented film. Further, in order to attain an improvement in the weatherability of the surface protective layer, it is possible to make the surface protective film such that it has an outermost surface deposited with SiO_x.

Description will be made of the surface side filler 203 (the transparent organic high-molecular resin layer).

The surface side filler 203 serves to cover the photovoltaic element with a given resin so as to protect it from the external environment. In addition, the surface side filler serves to bond the surface protective film with the photovoltaic element. Hence, the surface side filler is required to be highly transparent, and to excel in weatherability, adhesion, and heat resistance. In order for the surface side filler to meet these conditions, the surface side filler is desired to comprise a thermoplastic resin selected from the group consisting of polyolefinic resins, butyral resins, silicone resins, epoxy resins, and acrylic resins.

Preferable specific examples of such thermoplastic resin are ethylene-vinyl acetate copolymer (EVA), ethylene-methyl acrylate copolymer (EMA), ethylene-ethyl acrylate copolymer (EEA), ethylene-butyl acrylate copolymer (EBA), ethylene-methyl methacrylate copolymer (EMM), ethylene-ethyl methacrylate copolymer (EEM), and polyvinyl butyral (PVB). Of these resins, EVA and EEA are the most appropriate in view of acquisition easiness and from an economical viewpoint.

Any of the above mentioned resins usable as the surface side filler (this resin will be hereinafter referred to as filler resin) is low in heat deformation temperature and is liable to readily deform or creep at a high temperature. Because of this, the filler resin is desired to be crosslinked with an appropriate crosslinking agent so that it has an increased heat resistance and adhesion property. The crosslinking agent usable in this case can include isocyanates, melamines, and organic peroxides. In any case, the crosslinking agent used is desired to be such a crosslinking agent which has a sufficiently long pot life and quickly cases crosslinking reaction upon crosslinking the filler resin. Further, since the surface protective film is laminated on the surface side filler, it is desired for the crosslinking agent to be such a crosslinking agent that causes no free material from the crosslinking agent or only a slight amount of said free material.

In addition, the surface side filler may contain an antioxidant in order to prevent it from being thermally oxidized. Further in addition, in order to prevent the surface side filler from being deteriorated with light impinged, the surface side filler may contain an UV absorber or/and a light stabilizer.

In the case where the adhesion of the surface side filler with the photovoltaic element or the surface protective film is not sufficient enough, the adhesion can be improved by incorporating a silane coupling agent and a titanate coupling agent either singly or in combination into the surface side filler.

Description will be made of the transparent resin thin film layer 202 (or the transparent resin layer.

The transparent resin thin film layer 202 serves to coat the irregularities of the photovoltaic element with a given resin while protecting the photovoltaic element from the external environment in combination with the surface side filler. The transparent resin thin film layer 202 also serves to maintain the photovoltaic element in a state of being electrically isolated from the outside. As well as in the case of the surface side filler 203, the transparent resin thin film 202 is required to be highly transparent, and to excel in weatherability, adhesion, and heat resistance.

In order for the transparent resin thin film layer 202 to meet these conditions, the transparent resin thin film layer is comprised of a transparent resin selected from the group consisting of resins comprising acrylic resins, silicone resins, or fluororesins as a main constituent. Preferable specific examples of such resin are resins obtained by crosslinking an acrylic resin and an inorganic polymer with an appropriate crosslinking agent, silicone series resins such as alkoxysilazanes, and fluororesins.

The above acrylic resin can include resins obtained by polymerizing a methacrlic monomer selected from the group consisting of methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, methacrylic acid, diethylaminoethyl methacrylate, 2-hydroxyethyl methacrylate, tert-butylaminoethyl methacrylate, 2-hydroxypropyl methacrylate, dimethylaminoethyl methacrylate, ethylene dimethacrylate, ethylene glycol dimethacrylate, and 1,3-butylene dimethacrylate, and a monomer selected from the group consisting of isobutyl acrylate, acrylic acid diethyleneglycolethoxylate, 2-hydroxyethyl acrylate, and 2-hydroxypropylacrylate.

The above inorganic polymer can include polymers of silicon compounds such as siloxane, silazane, metallosiloxane, and metallosilazane and mixtures of these polymers.

As the crosslinking agent used for crosslinking the acrylic resin and inorganic polymer, it is desired to use a crosslinking agent which has a sufficiently long pot life and which quickly causes crosslinking reaction between the acrylic polymer and inorganic polymer to produce a crosslinked resin in a state containing no free material from the crosslinking agent or a slight amount of said free material if it should be contained.

There can be mentioned blocking isocyanates as the crosslinking agent which meets these conditions.

In terms of chemical structure of the isocyanate monomer for such blocking isocyanate, there can be mentioned tolylenediisocyanate, isophoronediisocyanate (IPDI), xylenediisocyanate (XDI), 1,3-bis(isocyanatomethyl)cyclohexane (H_6XDI), hexamethylenediisocyanate (HDI), tetramethylxylylenediisocyanate, and m-isopropenyl-α,α-dimethylbenzylisocyanate.

In the case where an excellent transparency is required, XDI which is of yellowing retardant type, and IPDI, H_6XDI and HDI which are of non-yellowing type are desired to be used.

The above mentioned isocyanate monomers are generally used as an isocyanate prepolymer. And they are roughly divided into adduct series of tetramethylene propanol (TMP) (or TMP adducts in other words), biuret series, isocyanurate series and alphanate series. In order for the transparent resin thin film layer to have an improved weatherability and heat resistance, a TMP adduct or isocyanurate is desired to be used.

As the blocking agent for the isocyanate, there can be mentioned oximes such as ethylacetoacetate and methyl ethyl ketone (MEK) oxime, lactams such as ε-caprolactam, phenols, and alcohols. In order to prevent a resin thin film as the transparent resin thin film layer from being yellowed upon the formation thereof or upon the use under condition with a high temperature, it is desired to use ε-caprolactam or alcohols.

In order to make a resin thin film as the transparent resin thin film layer to be desirably heat resistant when used under condition with a high temperature, the resin thin film may contain an antioxidant in an amount of 0.05 to 1.0 wt.% versus the total amount of the resin components of the resin film.

Such antioxidant can include monophenol series antioxidant, bisphenol series antioxidant, high-molecular phenol series antioxidant, sulphur series antioxidant, and phosphorous series antioxidant.

Specific examples of the monophenol series antioxidant are 2,6-di-tert-butyl-p-cresol, butylated hydroxyanisol, and 2,6-di-tert-butyl-4-ethylphenol.

Specific examples of the bisphenol series antioxidant are 2,2'-methylene-bis-(4-methyl-6-tert-butylphenol), 2,2'-methylene-bis-(4-ethyl-6-tert-butylphenol), 4,4'-thiobis-(3-methyl-6-tert-butylphenol), 4,4'-butylidene-bis-(3-methyl-6-tertbutylphenol), and 3,9-[1,1-dimethyl-2-{β-(3-tert-butyl-4-hydroxy-5-methylphenyl)propyonyloxy ethyl}2,4,8,10-tetraoxapyro]5,5 undecan.

Specific examples of the high-molecular phenol series antioxidant are 1,1,3-tris-(2-methyl-4-hydroxy-5-tert-butylphenyl)butane, 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene, tetrakis- methylene-3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate methane, bis 3,3'-bis-(4'-hydroxy-3'-tert-butylphenyl)butyric acid glucoseester, 1,3,5-tris(3',5'-di-tert-butyl-4'-hydoxylbenzyl)-s-triazine-2,4,6-(1H,3H,5H)trion, and tocopherol (Vitamin E).

Specific examples of the sulphur series antioxidant are dilaurylthiodipropionate, dimyristylthiodipropionate, and distearylthiopropionate.

Specific examples of the phosphorous series antioxidant are triphenylphosphate, diphenylisodecylphosphate, phenyldiisodecylphosphate, 4,4'-butylidene-bis-(3-methyl-6-tert-butylphenyl-ditridecyl)phosphate, cyclicneopentanetetrabis(octadecylphosphate), tris(mono or di)phenylphosphate, diisodecylpentaerythritoldiphosphate, 9,10-dihydro-9-oxa-10-phosphenanthrene-10-oxide, 10-(3,5-di-tert-butyl-4-hydroxybenzyl)-9,10-dihydro-9-oxa-10-phosphenanthrene-10-oxide, 10-decyloxy-9,10-dihydro-9-oxa-10-phosphenanthrene, cyclicneopentanetetrabis(2,4-di-tert-butylphenyl)phosphate, cyclicneopentanetetrabis(2,6-di-tert-methylphenyl)phosphate, and 2,2-methylenebis(4,6-tert-butylphenyl)octylphosphate.

These antioxidants may be used either singly or in combination of two or more of them.

Further, in order for the resin thin film as the transparent resin thin film layer to have an improved adhesion, the resin film may contain a silane coupling agent in an amount of 0.1 to 10 wt.% versus the total amount of the resin components of the resin film.

Such silane coupling agent in terms chemical structure can include compounds represented by the general formula $XSiY_3$, with X being a reactive organic functional group and Y being a hydrolyzable group. The reactive organic functional group X can include an amino group, γ-glycidoxypropyl group, vinyl group, methacryl group, mercapto group, and chlorine group. The hydrolyzable group Y can include alkoxy groups such as methoxy group and ethoxy group. Of these groups, γ-glycidoxypropyl group is the most appropriate as the group X, and methoxy group is the most appropriate as the group Y.

Specific examples of these compounds are γ-(2-aminoethyl)aminopropyltrimethoxysilane, γ-(2-aminoethyl)aminopropyldimethoxysilane, γ-methacryloxypropyltrimethoxysilane, γ-(2-aminoethyl)aminopropyltrimethoxysilane, γ-glycidoxypropyltrimethoxysilane, γ-mercaptopropyltrimethoxysilane, vinyltrimethoxysilane, hexamethyldisilazane, γ-allynynopropyltrimethoxysilane, and β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane.

Specifically, epoxy series silane coupling agents such as γ-glycidoxypropyltrimethoxysilane, γ-glycidoxypropyltriethoxysilane, and β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane are desired to be used. Of these, γ-glycidoxypropyltrimethoxysilane is the most desirable since its use as the silane coupling agent, an improvement can be attained in not only the adhesion but also the heat resistance of the resin thin film as the transparent resin thin film layer.

Further, the resin thin film as the transparent resin thin film layer may contain fine particles of an appropriate inorganic oxide (this will be hereinafter referred to as inorganic oxide fine particles).

Specific examples of such inorganic oxide are silicon oxide, zinc oxide, tin oxide, titanium oxide, and aluminum oxide.

The inorganic oxide fine particles added are desired to be of a mean particle size preferably in the range of from 1 μm to 1000 μm or more preferably in the range of from 5 μm to 100 μm.

As for the amount of the inorganic oxide fine particles to be added, when it is excessive, a problem is liable to entail in that light does not sufficiently arrive at the photovoltaic element. It is desired to be preferably in the range of from 0.1 wt.% to 20 wt.% or more preferably in the range of from 0.2 wt.% to 10 wt.%.

The incorporation of the inorganic oxide fine particles in a desired amount within the above range into the transparent resin thin film layer provides advantages such that incident light is desirably scattered to improve the photoelectric conversion efficiency, and the hardness of the transparent resin thin film layer is increased and as a result, the performance of the transparent resin thin film layer as the protective layer for the photovoltaic element is improved, wherein particularly, the weatherability of the transparent resin thin film layer is improved.

The incorporation of the inorganic oxide fine particles into the transparent resin thin film layer may be conducted by a manner of adding fine particles of any of the foregoing inorganic oxides to a given resin for the formation of the transparent resin thin film layer and forming a resin thin film as the transparent resin thin film layer or a manner of forming a resin thin film as the transparent resin thin film layer and spraying fine particles of any of the foregoing inorganic oxides onto the resin thin film.

Description will be made of the filler 205 (the backside filler) disposed on the rear side of the photovoltaic element 201.

The backside filler 205 serves to attain a sufficient adhesion between the photovoltaic element 201 and the back face protective film 206. The backside filler 205 is desired to comprise a material capable of sufficiently ensuring the adhesion between the electrically conductive substrate of the photovoltaic element and the back face protective film and which excels in durability, withstands a thermal expansion and thermal contraction, and excels in flexibility. Specific examples of such material are hot-melt materials such as EVA (ethylene-vinyl acetate copolymer) and polyvinyl butyral, and epoxy adhesives. Besides these, double-coated tapes may be also usable.

Alternatively, the backside filler 205 may comprise the same resin material used for the surface side filler 203.

When the solar cell module is one which is used under environmental condition with a high temperature, for instance, which is integrated to a roof of a building in order to use in outdoors, it is desired to use a material capable of being crosslinked as the backside fill in order to attain a further improved adhesion between the electrically conductive substrate of the photovoltaic element and the back face protective film so that the solar cell module can endure upon repeated use at high temperature. Incidentally, resin materials such as EVA can be desirably crosslinked with the use of an organic peroxide.

Description will be made of the back face protective film 206.

The back face protective film 206 is disposed for the purpose of electrically isolating the electrically conductive substrate of the photovoltaic element 201 from the outside. The back face protective film 206 is desired to be composed of a material which can sufficiently electrically isolating the electrically conductive substrate of the photovoltaic element, excels in durability, withstands a thermal expansion and thermal contraction, and excels in flexibility. Specific examples of such material are laminate films comprising a nylon film or a PET (polyethylene terephthalate) film, having an adhesive layer composed of a polyolefin resin on the both faces. The polyolefin resin can include ethylene-vinyl acetate copolymer (EVA), ethylene-methyl acrylate copolymer (EMA), and ethylene-ethyl acrylate copolymer (EEA).

In the present invention, it is possible to dispose a back face reinforcing member (not shown in the figure) outside the back face protective film 206 in order to improve the mechanical strength of the solar cell module and in order to prevent the solar cell module from being distorted or warped due to changes in the environmental temperature. The back face reinforcing member may comprise a steel plate, a plastic plate, or a fiber-glass reinforced plastic plate (or a so-called FRP plate).

Now, in order to prevent a decrease in the quantity of incident light to be arriving in the photovoltaic element, the surface covering material comprising the transparent resin thin film layer 202, the transparent surface side filler 203 and the surface protective film 204 which are stacked in the named order from the photovoltaic element side is desired to be substantially transparent. Specifically, it is desired for the surface covering material to have a transmittance of preferably 80% or more or more preferably 90% or more in a visible light wavelength region of 400 nm to 800 nm. Further, in order to facilitate external light to be readily impinged into the photovoltaic element, the surface covering material is made to be such that it has a refractive index of preferably 1.1 to 2.0 or more preferably 1.1 to 1.6 at a temperature of 25 °C.

In the following, description will be made of a manner of producing a solar cell module as a semiconductor device according to the present invention using the foregoing photovoltaic element (or photoelectric conversion element), transparent resin thin film layer, filler resin, surface protective film, and back face protective material.

To coat a light receiving face of the photovoltaic element by the transparent resin thin film layer may be conducted by applying a coating liquid comprising a given resin for the formation of the transparent resin thin film layer dissolved in an solvent. The application of the coating liquid onto the light receiving face of the photovoltaic element may be conducted by a manner of dipping the photovoltaic element in the coating liquid to form a coat film of covering the light receiving face of the photovoltaic element; a manner of air-spraying the coating liquid in an atomized state over the light receiving face of the photovoltaic element to form a coat film of covering the light receiving face of the photovoltaic element; or a manner air-spraying the coating liquid in the liquid state over the light receiving face of the photovoltaic element to form a coat film of covering the light receiving face of the photovoltaic element. In any case, the coat film formed on the photovoltaic element is subjected to crosslinking treatment while evaporating the solvent or after the solvent has been vaporized. Besides these manners, the formation of the transparent resin thin film layer on the photovoltaic element may be conducted by a manner of providing a given resin in a powdery form for the formation of the transparent resin thin film layer, depositing the powdery resin on the light receiving face of the photovoltaic element by way of electrostatic adsorption to form a coat film of covering the light receiving face of the photovoltaic element, and subjecting the coat film to heat treatment to crosslink it.

To coat the light receiving face of the photovoltaic element (particularly, the light receiving face of the solar cell element 207 (see, FIG. 2)) by the surface side filler may be conducted by (a) a manner of applying a coating liquid comprising a filler resin material dissolved in a solvent onto the light receiving face and vaporizing the solvent of the coating liquid applied; (b) a manner of uniformly depositing a powdery filler resin material on the light receiving face and subjecting the powdery filler resin material deposited to heat fusion; (c) a manner of providing a heat-fused product of a filler resin material and applying the heat-fused product onto the light receiving face through a slit; or (d) a manner of obtaining a sheet of a filler resin material using a heat-fused product of the filler resin material and laminating the sheet on the light receiving face by way of thermocompression bonding.

In the case of the above manner (a), if necessary, one or more of desired additives such as silane coupling agent, UV absorber, antioxidant and the like are firstly mixed with the solvent prior to dissolving the filler resin material therein, and the resultant coating liquid is applied onto the light receiving face of the photovoltaic element, follower by drying.

Similarly, in any of the remaining manners (b) to (d), in the case of using one or more of said desired additives, such additive is added to the filler resin material prior to heat-fusing the filler resin material.

In the case where the surface side filler 203 has been previously formed on the light receiving face of the solar cell element 207 (see, FIG. 2), the surface protective film 204 is laminated on the surface side filler and the back side filler resin material 205 and the back face protective film 206 are laminated on the rear face of the solar cell element to obtain a composite, and the resultant composite is subjected to thermocompression bonding, whereby a desirable solar cell module can be obtained. In the case where the back face reinforcing member is intended to dispose, it is possible for the back face reinforcing member to be laminated to the back face protective film by means of an appropriate adhesive. The lamination of the back face reinforcing member may be conducted upon conducting the above thermocompression bonding or it may be independently conducted after the above thermocompression bonding.

Alternatively, a sheet composed a filler resin material for the surface side filler may be used instead of the surface side filler having been previously formed on the light receiving face of the solar cell element in the above procedures. In this case, the sheet is interposed between the surface protective film and the solar cell element to obtain a composite, and the resultant composite is subjected to thermocompression bonding, whereby a desirable solar cell module can be obtained.

The thermocompression bonding can include vacuum lamination and roll lamination.

In the following, the present invention will be described in more detail with reference to examples which are not intended to restrict the scope of the present invention.

Example 1

1. Preparation of photoelectric conversion element (solar cell):

There were prepared a plurality of solar cells each having the configuration shown in FIG. 3 and which has a semiconductor active layer composed of an amorphous silicon material (that is, a-Si material) (this solar cell will be hereinafter referred to as a-Si solar cell) in the following manner.

That is, there was firstly provided a well-cleaned stainless steel plate as the substrate 301. On the substrate 301, there was formed a two-layered back reflecting layer 302 comprising a 500 nm thick Al film and a 500 nm thick ZnO film by means of the conventional sputtering process, followed by forming, on the back reflecting layer 302, a tandem type a-Si photoelectric conversion semiconductor layer 303 with a nip/nip structure comprising a 15 nm thick n-type layer/a 400 nm thick i-type layer/a 10 nm thick p-type layer/a 10 nm thick n-type layer/a 80 nm thick i-type layer/a 10 nm thick p-type layer being laminated in the named order from the substrate side by means of the conventional plasma CVD manner, wherein an n-type a-Si film as each n-type layer was formed from a mixture of SiH_4 gas, PH_3 gas and H_2 gas; an i-type a-Si film as each i-type layer was formed from a mixture of SiH_4 gas and H_2 gas; and a p-type μc-Si film as each p-type layer was formed from a mixture of SiH_4 gas, BF_3 gas and H_2 gas. Then, on the semiconductor active layer 303, there was formed a 70 nm thick transparent and conductive layer 304 composed of In_2O_3 by means of the conventional heat resistance evaporation process wherein an In-source was evaporated in an O_2 atmosphere. Thus, there was obtained a photovoltaic element.

The resultant photovoltaic element was found to have a shunt resistance of 1 $k\Omega.cm^2$ to 10 $k\Omega.cm^2$. Therefore, the photovoltaic element was subjected to defect-repairing treatment in the following manner. That is, the photovoltaic element and an electrode plate were immersed in a aqueous solution of aluminum chloride having adjusted to have an electric conductivity of 50 to 70 mS such that the electrode plate was opposed to the transparent and conductive layer of the photovoltaic element, and wherein the photovoltaic element was electrically grounded. Then, a positive electric potential of 3.5 V was impressed to the electrode plate for 2 seconds, whereby the transparent and conductive layer situated at shunted (or short-circuited) portions in the photovoltaic element was selectively decomposed. The photovoltaic element thus repaired was found to have a shunt resistance of 50 $k\Omega.cm^2$ to 200 $k\Omega.cm^2$.

Successively, a grid electrode as the collecting electrode 305 was formed on the transparent and conductive layer 304 in the following manner. That is, on the transparent and conductive layer, there was formed a Cu-paste line with a width of 200 um by means of screen printing. Then, a copper wire of 100 um in diameter was wired on and along the Cu-paste line, a cream solder was disposed thereon, followed by fusing the solder to thereby fix the copper wire onto the Cu-paste. By this, there was formed the grid electrode on the transparent and conductive layer.

As for the resultant, a copper tub as the negative side power outputting terminal 306b was fixed to the substrate 301 using a stainless solder, and a tin foil tape as the positive side power outputting terminal 306a was fixed to the grid electrode as the collecting electrode 305 using a solder. Thus, there was obtained an a-Si solar cell. In this way, there were obtained a plurality of a-Si solar cells.

2. Preparation of module:

Using each of the a-Si solar cells obtained in the above 1, there were prepared a plurality of solar cell modules each having the configuration shown in FIG. 4 in the following manner.

In FIG. 4, reference numeral 401 indicates a photoelectric conversion element (corresponding to the foregoing a-Si solar cell in this case), reference numeral 402 a transparent resin thin film layer disposed on the photoelectric conversion element 401 so as to cover a light receiving surface thereof, reference numeral 403 a filler (comprising a transparent organic high-molecular resin layer) which encloses a stacked body comprising the photoelectric conversion element 401 and the transparent resin thin film layer 402, reference numeral 404 a surface protective film disposed on the filler 403, reference numeral 405 a back face protective film disposed under the filler 403, and reference numeral 406 a back face reinforcing member disposed under the back face protective film. The filler 403 herein is meant to include a surface side filler and a backside filler.

(1) Preparation of a laminate comprising a transparent thin film layer 402 formed on a photoelectric conversion element 401 (that is, the a-Si solar cell obtained in the above) so as to cover the light receiving face:

100 parts by weight of a resin mixture composed of an acrylic resin, an inorganic polymer, and hexamethylenediisocyanate blocked by ε-caplolactam and 2.8 parts by weight of γ-methacryloxypropyltrimethoxysilane as a silane coupling agent to obtain a mixture. The mixture was applied onto the light receiving face of the a-Si solar cell by means of the conventional coating process to form a coat film, followed by subjecting the coat film to heat treatment to vaporize the solvent while crosslinking the resin of the coat film, to thereby form a transparent resin thin film as the transparent resin thin film layer 402 on the a-Si solar cell 401 so as to cover the light receiving face thereof. By this, there was obtained a laminate comprising the a-Si solar cell and the transparent thin film layer.

(2) Provision of a filler material as the filler 403:

(a) As the surface side filler, there was provided a 460 μm thick EVA sheet obtained by mixing a 100 parts by weight of EVA (ethylene-vinyl acetate copolymer), 3 parts by weight of 2,5-dimethyl-2,5-bis(t-butylperoxy)hexane as a crosslinking agent, 1.0 part by weight of -methacryloxypropyltrimethoxysilane as a silane coupling agent, 0.3 part by weight of 2-hydroxy-4-n-octoxybenzophenone as a UV absorber, 0.1 part by weight of bis(2,2,6,6-tetramethyl-4-peperidyl)sebacate as a light stabilizer, and 0.2 part by weight of tris(monononylphenyl)phosphate as an antioxidant were mixed to obtain a mixture, subjecting the mixture to heat fusing to obtain a fused product, and subjecting the fused product to extrusion molding using a T-die wherein the fused product was extruded through the slit of the T-die.

(b) As a backside filler, there was provided a 460 μm thick EVA film.

(3) Provision of a film as the surface protective film 404:

As the surface protective film 404, there was provided a 38 um thick stretched ETFE film having a surface treated by way of corona discharging which is to be contacted with the surface of the filler 403 (the surface side filler).

(4) Provision of a film as the back face protective film 405:

As the back face protective film 405, there was provided a laminate film comprising an EEA (ethylene-ethyle acrylate copolymer) film of 200 um in thickness/a polyethylene film of 25 um in thickness/a PET (polyethylene terephthalate) film of 50 um in thickness/an EEA (ethylene-ethyle acrylate copolymer) film of 200 um in thickness.

(5) Provision of a member as the back face reinforcing member 406:

As the back face reinforcing member 406, there was provided a 0.3 mm thick galvalume steel member (or a Zn-coated steel member).

(6) Preparation of a solar cell module:

On the light receiving face of the laminate (that is, on the surface of the transparent resin thin film layer disposed on the a-Si solar cell) obtained in the above (1), there were laminated the EVA sheet (obtained in the above (2)-(a)) and the the ETFE film (provided in the above (3)) in the named order. In this case, the corona-discharged surface of the ETFE film was contacted with the surface of the EVA sheet. On the rear face of the resultant, there were laminated the EVA film (provided in the above (2)-(b)), the laminate film (provided in the above (4)) and the galvalume steel member (provided in the above (5)) in the named order. Thus, there was obtained a stacked body. The stacked body thus obtained was placed in a vacuum laminator, wherein it was subjected to heat treatment at 150 °C for 30 minutes while evacuating the inside of the vacuum vessel to a predetermined vacuum degree, followed by cooling to room temperature. Thus, there was obtained a solar cell module.

In this way, there were prepared a plurality of solar cell modules.

Evaluation

Using the resultant solar cell modules, evaluation was conducted with respect to combustibility, heat resistance, adhesion, endurance against changes in environmental temperature, weatherability, electrical insulation, and resistance to scratching.

The evaluated results obtained are collectively shown in Table 1.

The evaluation of each of the above evaluation items was conducted in the following manner.

(1) Evaluation of the combustibility:

The solar cell module was placed on a deck slanted at 22° against the horizon. And a gas burner flame of 760± 28 °C was supplied to the surface covering material side of the solar cell module for 10 minute, wherein the fame spreading was observed. The observed result is shown in Table 1 based on the following criteria:

○ : a case where the flame spreading is less than a distance of 6 feet from the tip, and
X a case where the flame spreading is beyond a distance of 6 feet from the tip.

(2) Evaluation of the heat resistance:

The solar cell module was exposed to an atmosphere of 150 °C for 15 hours, and thereafter, a change in the initial transmittance of its surface covering material against light of 400 nm in wavelength was observed. The observed result

◎is shown in Table 1 based on the following criteria:

○ : a case where no yellowing is occurred (the change in the initial transmittance is less than 10%), and
X : a case where yellowing is occurred (the change in the initial transmittance is greater than 10%).

(3) Evaluation of the adhesion:

As for the solar cell module, in accordance with the manner based on the JIS K5400 8.5.2, the adhesion between the transparent resin thin film layer and the transparent and conductive layer was examined. The examined result is shown in Table 1 based on the following criteria:

○ : a case where no separation is occurred, and
X : a case where a separation is occurred.

(4) Evaluation of the endurance against changes in environmental temperature:

The solar cell module was subjected to alternate repetition of a cycle of exposing to an atmosphere of - 40 °C for an hour and a cycle of exposing to an atmosphere of 85 °C/85 %RH for an hour 20 times, and thereafter, its exterior appearance was optically observed. The observed result is shown in Table 1 based on the following criteria:

◎: a case where no change is observed in the exterior appearance,
○ : a case where a slight change is observed in the exterior appearance but it is not problematic in practice, and
X : a case where problematic, distinguishable removal or/and crack, and coloring which are not acceptable in practice are observed in the exterior appearance.

(5) Evaluation of the weatherability:

The solar cell module was placed in a carbon-arc sunshine weather meter, wherein it was irradiated with pseudo sunlight for 5000 hours under conditions of alternately repeating a cycle of maintaining at a black panel temperature of 63 °C for 108 minutes and a cycle of pure water fall for 12 minutes. Thereafter, its exterior appearance was optically observed. The observed result is shown in Table 1 based on the following criteria:

◎ : a case where no change is observed in the exterior appearance,
○ : a case where a slight change is observed in the exterior appearance but it is not problematic in practice, and
X : a case where problematic, distinguishable removal or/and crack, and coloring which are not acceptable in practice are observed in the exterior appearance.

(6) Evaluation of the electrical insulation:

As for the solar cell module, the plus and minus poles were intentionally short-circuited. A high-pot tester was electrically connected between the short-circuited terminal and the back face reinforcing member and 2200 DC voltage was impressed, wherein a leakage current was measured. The measured result is shown in Table 1 based on the following criteria:

○ : a case (acceptable) where the leakage current is 50 μA or less, and
X : a case (not acceptable) where the leakage current is beyond 50 μA.

(7) Evaluation of the resistance to scratching:

This evaluation was conducted in the following manner. That is, the solar cell module was subjected to surface treatment in a manner shown in FIG. 5, wherein a 1 mm thick metal plate 602 is contacted through a corner thereof to the most recessed portion of the light receiving surface side 601 of the solar cell module. Then, to the metal plate, a load F of 2 pounds is applied and a load F of 5 pounds is applied without moving the metal plate. Then the metal plate is pulled in a direction indicated by an arrow D while applying the latter load thereto to form a scratch. Then the solar cell module thus treated is evaluated of whether or not its scratched portion of the surface covering material is still insulative in electrically isolating from the outside. This evaluation is conducted by immersing the treated solar cell module in an electrolytic solution of 3000Ω .cm, and applying a voltage of 2200 V between the photovoltaic element of the solar cell module and the electrolytic solution to observe a leakage current occurred. The evaluated result is shown in Table 1 based on the following criteria.

○:	a case (acceptable) where the leakage current is 50 μA or less, and
X :	a case (not acceptable) where the leakage current beyond 50 μA.

Example 2

The procedures of Example 1 were repeated, except that the isocyanate monomer used in the formation of the transparent resin thin film layer in Example 1 was replaced by 1,3-bis(isocyanatomethyly)cyclohexane, to thereby obtain a plurality of solar cell modules.

Using the resultant solar cell modules, evaluation was conducted in the same evaluation manner as in Example 1. The evaluated results obtained are collectively shown in Table 1.

Example 3

The procedures of Example 1 were repeated, except that the EVA used as the surface side filler in Example 1 was replaced by EEA (ethylene-ethyl acrylate copolymer), to thereby obtain a plurality of solar cell modules.

Using the resultant solar cell modules, evaluation was conducted in the same evaluation manner as in Example 1. The evaluated results obtained are collectively shown in Table 1.

Example 4

The procedures of Example 1 were repeated, except that the silane coupling agent used in the formation of the transparent resin thin film layer in Example 1 was replaced by γ-methacryloxypropyltrimethoxysilane, to thereby obtain a plurality of solar cell modules.

Using the resultant solar cell modules, evaluation was conducted in the same evaluation manner as in Example 1. The evaluated results obtained are collectively shown in Table 1.

Example 5

The procedures of Example 1 were repeated, except that the ε-caplolactam used as the blocking agent for the isocynate monomer in the formation of the transparent resin thin film layer in Example 1 was replaced by methyl ethyl ketone oxime, to thereby obtain a plurality of solar cell modules.

Using the resultant solar cell modules, evaluation was conducted in the same evaluation manner as in Example 1. The evaluated results obtained are collectively shown in Table 1.

Example 6

The procedures of Example 1 were repeated, except that the silane coupling agent used in the formation of the transparent resin thin film layer in Example 1 was replaced by γ-glycidoxypropyltrimethoxysilane, to thereby obtain a plurality of solar cell modules.

Using the resultant solar cell modules, evaluation was conducted in the same evaluation manner as in Example 1. The evaluated results obtained are collectively shown in Table 1.

Example 7

The procedures of Example 1 were repeated, except that fine particles of silicon oxide having a mean particle size of 10 μm were additionally used in the formation of the transparent resin thin film layer in Example 1, to thereby obtain a plurality of solar cell modules.

Using the resultant solar cell modules, evaluation was conducted in the same evaluation manner as in Example 1. The evaluated results obtained are collectively shown in Table 1.

Comparative Example 1

The procedures of Example 1 were repeated, except that no silane coupling agent was used in the formation of the transparent resin thin film layer in Example 1, to thereby obtain a plurality of solar cell modules.

Using the resultant solar cell modules, evaluation was conducted in the same evaluation manner as in Example 1. The evaluated results obtained are collectively shown in Table 1.

Comparative Example 2

The procedures of Example 1 were repeated, except that the transparent thin film layer used in Example 1 was replaced by a 460 µm thick EVA film, to thereby obtain a plurality of solar cell modules.

Using the resultant solar cell modules, evaluation was conducted in the same evaluation manner as in Example 1. The evaluated results obtained are collectively shown in Table 1.

Comparative Example 3

The procedures of Example 1 were repeated, except that the transparent thin film layer used in Example 1 was not used, to thereby obtain a plurality of solar cell modules.

Using the resultant solar cell modules, evaluation was conducted in the same evaluation manner as in Example 1. The evaluated results obtained are collectively shown in Table 1.

Table 1

	combustibility	heat resistance	adhesion	endurance against changes in environmental temperature	weatherability	electrical insulation	resistance to scratching
Example 1	○	○	○	◎	◎	○	○
Example 2	○	○	○	◎	◎	○	○
Example 3	○	○	○	◎	◎	○	○
Example 4	○	○	○	○	◎	○	○
Example 5	○	○	○	○	○	○	○
Example 6	○	○	○	○	○	○	○
Example 7	○	○	○	○	◎	○	◎
Comparative Example 1	○	X	X	X	X	X	X
Comparative Example 2	X	X	-	○	○	○	○
Comparative Example 3	○	○	-	○	○	X	X

Based on the results shown in Table 1, the following facts are understood. That is, by using a specific transparent resin film layer containing a silane coupling agent, particularly, an epoxy series silane coupling agent and diminishing the amount of EVA used, there can be attained a highly reliable surface covering material for a semiconductor element (specifically, a photoelectric conversion element), in which said transparent resin thin film layer always secures a sufficient adhesion with not only the transparent electrode of the semiconductor element but also the transparent organic resin layer situated above the transparent resin thin film layer even under environmental condition with a high temperature and which is always maintained in a desirable state without being yellowed even upon repeated used under severe environmental conditions with a high temperature and a high humidity.

By the way, as for a surface covering material having a transparent resin thin film layer formed using ε-caprolactam but using no epoxy series silane coupling agent, it is liable to yellow upon repeated use under environmental condition with a high temperature. As for the reason for this, it is considered that EVA contained in the surface covering material liberates acetic acid when it is oxidized and deteriorated and the acetic acid thus liberated reacts with ε-caprolactam remained in the transparent resin thin film layer to yellow the surface covering material. However, the incorporation of the epoxy series silane coupling agent into the transparent resin thin film layer eliminates the occurrence of the yellowing problem. That is, the epoxy series silane coupling agent functions to trap said acetic acid liberated, whereby the yellowing problem is effectively prevented from occurring.

Further, even in the case where EEA is used instead of EVA, no acid generation is occurred in acid decomposition reaction of the EEA. This also prevent the surface covering material from being yellowed. However, in the case of using methyl ethyl ketone oxime (that is, MEK oxime), although there can be found an effect of preventing the surface covering material from being yellowed, there is a tendency of entailing a drawback such that during the process of forming a coat film by way of heat treatment, the MEK oxime decomposes to produce a highly reactive nitrogen compound and because of this, the probability for the surface covering material to be yellowed is greater than that in the case of using -caprolactam and upon repeated use over a long period of time, the surface covering material is liable to yellow.

Further, as apparent from the evaluation results obtained in the endurance test against changes in environmental temperature and the environment resistance tests including the weatherability test, it is understood that any of the solar cell modules obtained in the examples belonging to the present invention is free of the occurrence of a separation in the stacked body and maintains its original exterior appearance without being damaged. In addition, as for the electrical insulation, any of the solar cell modules obtained in the examples belonging to the present invention has an excellent initial state in terms of electrical insulation from the outside and even after various endurance tests, still maintains in a satisfactory electrical insulation state.

Hence, it is understood that any of the solar cell modules obtained in the examples belonging to the present invention excels in module characteristics and can be safely repeatedly used over a long period of time and therefore, is highly reliable.

As apparent from the above description, according to the present invention, in a semiconductor device such as a solar cell module in which at least the incident light side surface of a semiconductor element is sealed by a transparent resin layer and at least a transparent organic high-molecular resin layer, by incorporating into the transparent resin layer a silane coupling agent, particularly, a compound represented by the general formula $XSiY_3$ with X being a reactive organic functional group and Y being a hydrolyzable group, there can be attained a highly reliable surface covering material which is hardly deformed and hardly peeled and excels in heat resistance even upon repeated use under such severe environmental conditions that the solar cell module is heated to a high temperature with repeated irradiation of direct sunlight in outdoors. In addition, there can be attained a highly reliable surface covering material for a solar cell module which is hardly yellowed and excels in heat resistance and which therefore effectively maintain the solar cell characteristics in a desirable state without being deteriorated even upon repeated use under severe environmental conditions with a high temperature and a high humidity.

A highly reliable surface covering material having a specific transparent resin layer formed of a resin containing a silane coupling agent in a state with no free material of said silane coupling agent for a semiconductor element or a semiconductor device, which is free of the occurrence of a separation, has a satisfactory heat resistance, and is hardly yellowed, and which enables the semiconductor element or semiconductor device to effectively its characteristics without being deteriorated, even when repeatedly used over a long period of time under severe environmental conditions with a high temperature and a high humidity.

Claims

1. A protective material including a transparent resin layer for a semiconductor element, said protective material being formed of a resin containing a silane coupling agent in a state with no free material of said silane coupling agent.

2. A protective material according to claim 1, wherein the silane coupling agent includes a compound represented by the general formula $XSiY_3$ with X being a reactive organic functional group and Y being a hydrolyzable group.

3. A protective material according to claim 1, wherein the silane coupling agent includes an epoxy series silane coupling agent.

4. A protective material according to claim 1 which is crosslinked by an isocyanate.

5. A protective material according to claim 1 which contains an acrylic resin.

6. A protective material according to claim 1 which contains an acrylic resin as a main component.

7. A protective material according to claim 1 which contains a resin formed by crosslinking an acrylic resin and an inorganic polymer.

8. A protective material according to claim 1 which contains a resin formed by crosslinking an acrylic resin and an inorganic polymer as a main component.

9. A protective material according to claim 4, wherein the isocynate monomer comprises at least either hexamethylenediisocyanate or 1,3-bis(isocyanatomethyl)cyclohexane.

10. A protective material according to claim 4, wherein the isocynate has an isocyanate group masked by ε-caprolactam.

11. A protective material according to claim 3, wherein the epoxy series silane coupling agent comprises at least a member selected from the group consisting of γ-gylcidoxypropyltrimethoxysilane γ-gylcidoxypropyltriethoxysilane, and β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane.

12. A protective material according to claim 1, wherein the semiconductor element is a photoelectric conversion element.

13. A protective material according to claim 12, wherein the photoelectric conversion element is a solar cell element.

14. A semiconductor element having a protective material including a transparent resin layer, said transparent resin layer being formed of a resin containing a silane coupling agent in a state with no free material of said silane coupling agent.

15. A semiconductor element according to claim 14, wherein the silane coupling agent includes a compound represented by the general formula $XSiY_3$ with X being a reactive organic functional group and Y being a hydrolyzable group.

16. A semiconductor element according to claim 14, wherein the silane coupling agent includes an epoxy series silane coupling agent.

17. A semiconductor element according to claim 14, wherein the transparent resin layer is crosslinked by an isocyanate.

18. A semiconductor element according to claim 14, wherein the transparent resin layer contains an acrylic resin.

19. A semiconductor element according to claim 14, wherein the transparent resin layer contains an acrylic resin as a main component.

20. A semiconductor element according to claim 14, wherein the transparent resin layer contains a resin formed by crosslinking an acrylic resin and an inorganic polymer.

21. A semiconductor element according to claim 14, wherein the transparent resin layer contains a resin formed by crosslinking an acrylic resin and an inorganic polymer as a main component.

22. A semiconductor element according to claim 17, wherein the isocynate monomer comprises at least either hexamethylenediisocyanate or 1,3-bis(isocyanatomethyl)cyclohexane.

23. A semiconductor element according to claim 17, wherein the isocynate has an isocyanate group masked by ε-caprolactam.

24. A semiconductor element according to claim 16, wherein the epoxy series silane coupling agent comprises at least a member selected from the group consisting of γ-gylcidoxypropyltrimethoxysilane γ-gylcidoxypropyltriethoxysilane, and β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane.

25. A semiconductor element according to claim 14 which is a photoelectric conversion element.

26. A semiconductor element according to claim 25, wherein the photoelectric conversion element is a solar cell element.

27. A semiconductor device having a protective material including a transparent resin layer and at least a transparent organic resin layer disposed on said transparent resin layer, said transparent resin layer being formed of a resin containing a silane coupling agent in a state with no free material of said silane coupling agent.

28. A semiconductor device according to claim 27, wherein the silane coupling agent includes a compound represented by the general formula $XSiY_3$ with X being a reactive organic functional group and Y being a hydrolyzable group.

29. A semiconductor device according to claim 27, wherein the silane coupling agent includes an epoxy series silane coupling agent.

30. A semiconductor device according to claim 27, wherein the transparent resin layer is crosslinked by an isocyanate.

31. A semiconductor device according to claim 27, wherein the transparent resin layer contains an acrylic resin.

32. A semiconductor device according to claim 27, wherein the transparent resin layer contains an acrylic resin as a main component.

33. A semiconductor device according to claim 27, wherein the transparent resin layer contains a resin formed by crosslinking an acrylic resin and an inorganic polymer.

34. A semiconductor device according to claim 27, wherein the transparent resin layer contains a resin formed by crosslinking an acrylic resin and an inorganic polymer as a main component.

35. A semiconductor device according to claim 30, wherein the isocynate monomer comprises at least either hexamethylenediisocyanate or 1,3-bis(isocyanatomethyl)cyclohexane.

36. A semiconductor device according to claim 30, wherein the isocynate has an isocyanate group masked by ε-caprolactam.

37. A semiconductor device according to claim 29, wherein the epoxy series silane coupling agent comprises at least a member selected from the group consisting of γ-gylcidoxypropyltrimethoxysilane γ-gylcidoxypropyltriethoxysilane, and β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane.

38. A semiconductor device according to claim 27, wherein the organic resin layer comprises a resin selected from the group consisting of thermoplastic polyolefin resins.

39. A semiconductor device according to claim 27, wherein the organic resin layer comprises a resin selected from the group consisting of ethylene-vinyl acetate copolymer and ethylene-ethyl acrylate copolymer.

40. A semiconductor device according to claim 28, wherein the X and Y of the general formula $XSiY_3$ are respectively a glicidoxypropynyl group and an alkoxy group.

41. A semiconductor device according to claim 28, wherein the transparent resin layer is a layer formed by means of a film-coating process.

42. A semiconductor device according to claim 27 which has a semiconductor element comprising a semiconductor active layer formed on an electrically conductive substrate as a first electrode and a transparent and conductive layer as a second electrode.

43. A semiconductor device according to claim 42, wherein the semiconductor active layer comprises a non-single crystal semiconductor thin film.

44. A semiconductor device according to claim 42, wherein the non-single crystal semiconductor thin film is composed of an amorphous silicon material.

45. A semiconductor device according to claim 27 which is a solar cell module.

F I G. 1

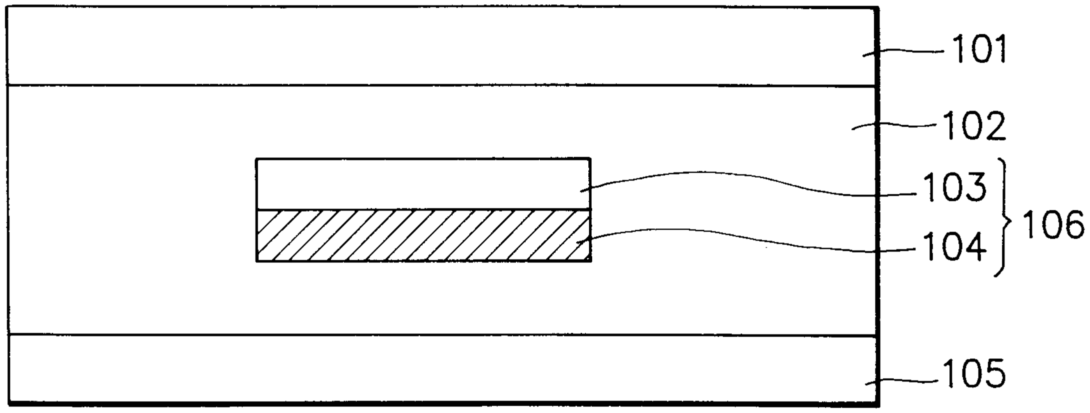

FIG. 2

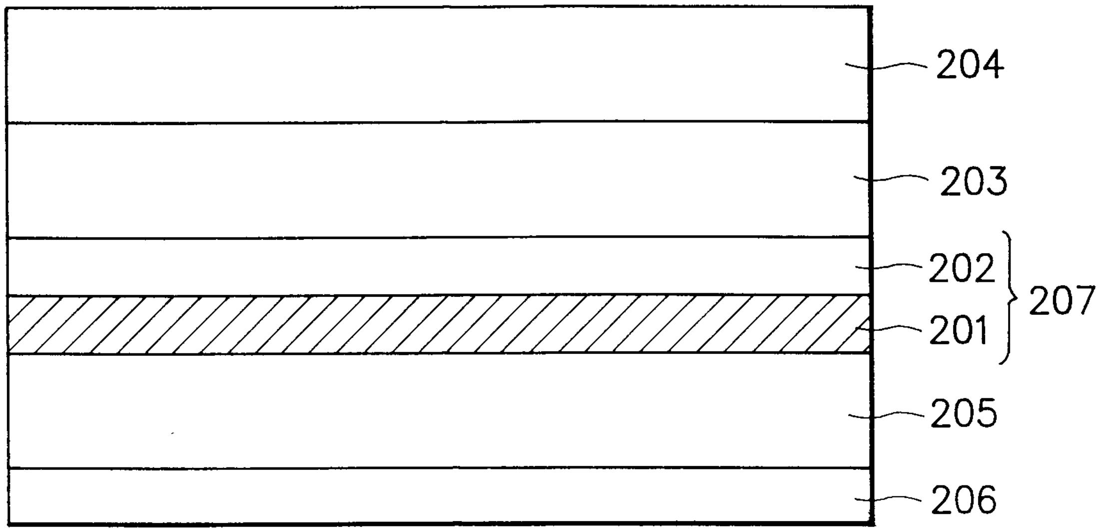

FIG. 3

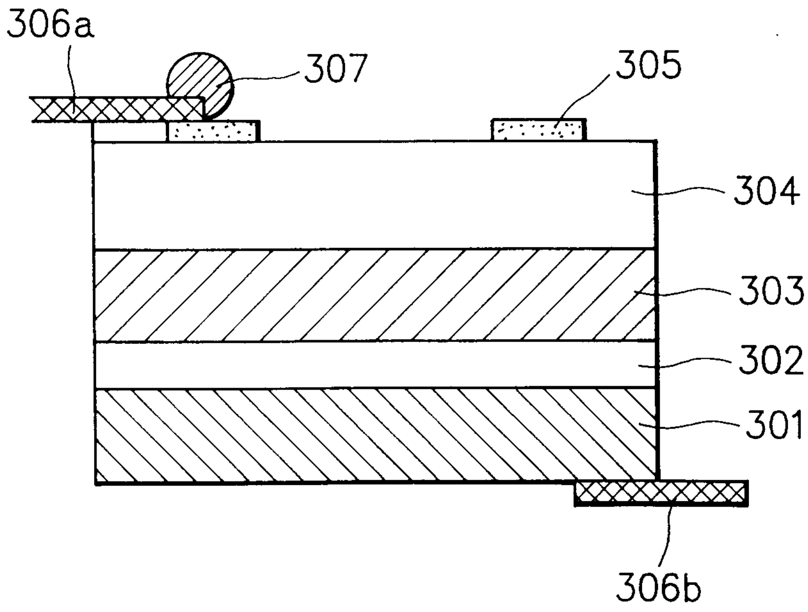

FIG. 4

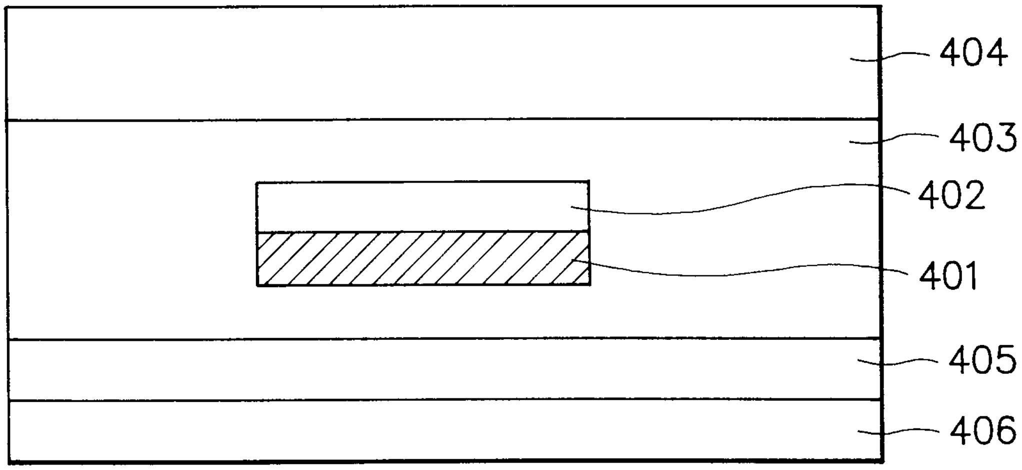

FIG. 5